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Nov 30, 1982

PUB-NO: JP357195122A
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TITLE: POLYPHENYLENE ETHER BLOCK COPOLYMER

PUBN-DATE: November 30, 1982

INVENTOR-INFORMATION:

NAME

COUNTRY

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ASSIGNEE-INFORMATION:

NAME

COUNTRY

MITSUBISHI PETROCHEM CO LTD

APPL-NO: JP56079573

APPL-DATE: May 26, 1981

US-CL-CURRENT: 528/195

INT-CL (IPC): C08G 65/48; C08L 71/00

ABSTRACT:

PURPOSE: To prepare the titled copolymer having improved moldability and impact resistance without lowering the excellent electrical properties, mechanical properties and thermal stability of the original resin, by reacting a polyphenylene ether with an aliphatic dialcohol through an aromatic dicarboxylic acid.

CONSTITUTION: The objective block copolymer of formula (R1 is H, halogen, hydrocarbon group, halohydrocarbon group, or hydrocarbon-oxy group; R2 is 5~20C alkylene or polyalkylene ether having a molecular weight of $\leq 2,000$; m is integer of 0~4; n is integer of 1~100; x and y are integers of 50~250) is obtained by the polycondensation reaction of (A) a polyphenylenen ether[e.g. poly(2,6-dimethyl-1,4-phenylene) ether]with (B) an aliphatic dialcohol (e.g. polytetramethylene glycol) and (C) an aromatic dicarboxylic acid compound (e.g. terephthaloyl dichloride).

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⑮ ポリフェニレンエーテルブロック共重合体

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⑯ 特 願 昭56—79573

⑰ 発 明 者 田山利行

⑱ 出 願 昭56(1981)5月26日

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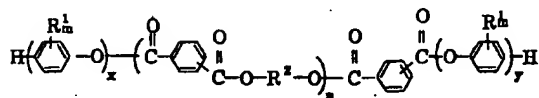
明 細 書

発明の名称

ポリフェニレンエーテルブロック共重合体

特許請求の範囲

一般式



(但し、ここでR¹は各々独立して水素原子、ハロゲン原子、炭化水素残基、ハロ炭化水素残基、炭化水素オキシ基およびハロ炭化水素オキシ基から選ばれたものであり、R²は炭素数5～20のアルキレン基または分子量2000以下のポリアルキレンポリエーテルを表わし、mは置換度であつて0～4の整数を、また、nは1～100の整数を表わし、xおよびyはポリフェニレンエーテルの重合度であつて50～250の整数を表わす。)で表わされるポリフェニレンエーテルブロック共重合体。

発明の詳細な説明

(I) 発明の背景

技術分野

本発明は改良された物性を有するポリフェニレンブロック共重合体に関する。

ポリフェニレンエーテル樹脂は電気的性質及び機械的性質が優れ、且つ高い熱変形温度を有するため、極めて有用なエンジニアリングプラスチック材料として注目されている。しかしながら、熔融温度が高く、且つ高温下での熱安定性に問題があるため、熔融下での成型加工を困難としている。

先行技術

ポリフェニレンエーテル樹脂の成型加工性を改善する一つの方法としては、他樹脂とのブレンドが試みられている。例えば特公昭43-17812号公報には、ポリフェニレンエーテルとバインバクトポリスチレンとのブレンドについて記載されている。このようなブレンド物は、ポリフェニレンエーテル樹脂の成型加工性と耐衝撃性を改善することができ、ノリルという商品名で市販され

ている。しかしながら、成型加工性はまだ充分であるとは言えない。

ポリフェニレンエーテル樹脂の成型加工性を改善するもう一つの方法としては、可塑剤の添加が検討されている。例えば特公昭49-5220号公報には、ポリフェニレンエーテル樹脂と良好な相溶性を有する芳香族有機酸エステル、芳香核を有するポリエステル、芳香核を有する有機リン酸エステル、塩素化芳香族炭化水素から選ばれる化合物をポリフェニレンエーテルまたはポリフェニレンエーテルとポリスチレンとよりなるブレンド物に添加することにより、成型加工性を改善している。この場合可塑剤の添加により、成型加工性は改良されるが、熱的性能が著しく低下することとなる。

(B) 発明の概要

目 的

本発明者等は、ポリフェニレンエーテル樹脂の有する優れた性能をできるだけ損なうことなく、成型加工性を改良する方法について鋭意検討した

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の整数を表わす。)。

効 果

本発明のポリフェニレンエーテルブロック共重合体はポリフェニレンエーテル樹脂が本来保有する優れた諸物性をできるだけ損うことなく成形加工性が改善されると共に機械的強度、特に衝撃強度においては従来のポリフェニレンエーテル樹脂よりも改良される。

(四) 発明の具体的説明

1. ポリフェニレンエーテルブロック共重合体

(i) 製造方法

本発明のポリフェニレンエーテルブロック共重合体は、ポリフェニレンエーテルと脂肪族ジアルコールを芳香族ジカルボン酸を介して反応させることにより容易に製造することができる。

(a) 構成成分

ポリフェニレンエーテル

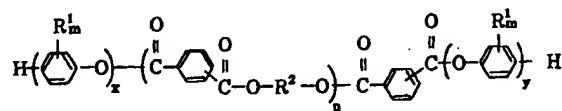
上記ポリフェニレンエーテルブロック共重合体に用いられるポリフェニレンエーテルは一般に下記の式で表わすことができる。

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結果、下記構造を有するポリフェニレンエーテルブロック共重合体がポリフェニレンエーテル樹脂と比して著しく成型加工性が改良されることを見出した。さらに驚くべきことには機械的強度の内、特に衝撃強度においても改良効果が認められた。

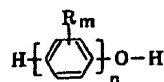
要 旨

即ち、本発明は一般式



なる構造を有するポリフェニレンエーテルブロック共重合体に関するものである(式中R¹は各々独立して水素原子、ハロゲン原子、炭化水素残基、ハロ炭化水素残基、炭化水素オキシ基およびハロ炭化水素オキシ基から選ばれたものであり、R²は炭素数5~20のアルキレン基または分子量2000以下のポリアルキレンポリエーテルを表わし、mは置換度数であつて0~4の整数を、また、nは1~100の整数を表わし、xおよびyはポリフェニレンエーテルの重合度であつて50~250

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ここで置換基R¹はそれぞれ独立に水素、ハロゲン原子、炭化水素残基(特にC₁~C₁₂のアルキル基)、ハロ炭化水素残基(特にC₁~C₁₂のハロアルキル基)、炭化水素オキシ基(特にC₁~C₁₂のアルキルオキシ基)、またはハロ炭化水素オキシ基(特にC₁~C₁₂のハロアルキルオキシ基で、この基が結合すべきフェニル基とハロゲンとの間になくとも2個の炭素原子が存在することが好ましい。)である。これらの基の炭化水素ないし炭化水素部分は第三-α-炭素原子を持たないことが好ましい。mは置換度であつて最高4の整数である。nは重合度であつて50~250、好ましくは100~200である。ポリフェニレンエーテル及びその製造法自身は本発明とは無関係であり、必要に応じて各種の文献たとえば米国特許第3,257,357号、同第3,306,687号等各明細書を参照することができる。ポリフェニレンエ

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n が 1 のものである。

第三の方法はポリフェニレンエーテルと脂肪族ジアルコールの共存下、芳香族ジカルボン酸の酸クロライドを反応させて得ることができる。

第二、第三の方法においても第一の方法と同様に芳香族ジカルボン酸の酸クロライドのかわりに芳香族ジカルボン酸のジメチルエステルあるいは芳香族ジカルボン酸をそのまま用いることができる。

ポリフェニレンエーテルブロック共重合体の製造法としては、上記三つの方法のいずれを用いても良いが、第三番目の方法は、前二方法と比較し、分子 $\frac{M_w}{M_n}$ 分布が広がる傾向がある。

反応条件としては、反応中間体を製造する工程及び、ポリフェニレンエーテルブロック共重合体を製造する工程とも、テレフタル酸クロライドを用いる場合には、ベンゼンの如き可溶性溶剤のもとで、30～100℃の温度で、1～8時間攪拌することにより得ることができる。この際必要に応じてピリジン、トリエチルアミン等のアミン類

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を要し、x および y はポリフェニレンエーテルの重合度であつて 50～250 の整数を表わす。) で表わされる共重合体である。

上記式中の x および y はポリフェニレンエーテルの重合度で 50～250、好ましくは 100～200 の整数を表わし、50 未満ではポリフェニレンエーテルの特徴の一つである電気的特性が悪化する。また、250 を越える場合は成形性の改良が損なわれる。

さらに、n は 1～100 の整数を表わすが、100 を越える場合は耐熱性が損なわれる。また、R²がポリアルキレンポリエーテルの場合は分子量が 2000 以下、好ましくは 500～1000 のポリアルキレンポリエーテルを用いるのが良い。

3. その他の樹脂とのブレンド

このようなポリフェニレンエーテルブロック共重合体を単独で用いるかポリスチレン系重合体とブレンドして用いるか、或いはポリフェニレンエーテルとポリスチレン系重合体よりなる樹脂組成物とブレンドして用いることができる。

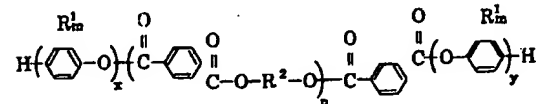
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を用いても良い。

2. ブロック共重合体の特性

このようにして得られたポリフェニレンエーテルブロック共重合体は、ポリフェニレンエーテル樹脂の優れた諸物性を著しく損うことなく成形加工性を顕著に改善されたものであると共に機械的強度、特に衝撃強度を顕著に改善されたものである。

本発明のポリフェニレンエーテルブロック共重合体は一般式、



(但し、ここで R は各々独立して水素原子、ハロゲン原子、炭化水素残基、ハロ炭化水素残基、炭化水素オキシ基およびハロ炭化水素オキシ基から選ばれたものであり、R²は炭素数 5～20 のアルキレン基または分子量 2000 以下のポリアルキレンポリエーテルを表わし、m は置換度であつて 0～4 の整数を、また、n は 1～100 の整数

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本発明の共重合体は成形加工性が改良されたため、単独使用することも可能であるが、経済的にはポリスチレン系重合体と混合することが有利である。

また、本発明のポリフェニレンエーテルブロック共重合体は他の添加剤、例えば可塑剤、顔料、難燃剤、補強剤例えばガラスフィラメントまたは繊維、安定剤などを含有させることができる。

以下の実施例により本発明をさらに具体的に説明する。

実施例-1

ポリエステル中間体の製造

両末端 OH のポリテトラメチレングリコール (MW 2080) を 10 倍モルのテレフタル酸ジクロライドと 50℃、1 時間ついで 120℃、30 分間、発生する塩酸ガスを窒素で追い出しながら反応させた。反応終了後、過剰のテレフタル酸ジクロライドを真空下、100℃以下で除去し、ポリテトラメチレングリコール-テレフタル酸クロライド反応物を得た。この反応物は GPC 解析及

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び水で処理した後の中和当量よりポリテトラメチレングリコール/テレフタル酸ジクロライドの $\frac{1}{2}$ 反応物であることを確認した。

ブロック共重合体の製造

(η) 0.46 (30℃クロロホルム) (\overline{M}_n 23,000) のポリフェニレンエーテル100gと脱水したベンゼン500mlをとり窒素雰囲気下50℃で攪拌溶解した。これに上記反応物5.31g (2.20ミリモル) と脱水したビリジン0.70g (8.80ミリモル) を加えた後50℃で1時間攪拌、反応した。反応終了後、メタノールにて再沈し、洗浄、乾燥してポリフェニレンエーテルブロック共重合体を得た。このものの(η)は0.58であつた。

物性測定

プレスにて試験片を作成し、18.6Kg荷重での熱変形温度を測定したところ183℃であり、デュボン衝撃強度(尖端に撃芯(12.5% ϕ)と凹みをもつ撃芯受台との間に試験用シート(厚み0.6mm)をおき、一定の重錘(300g)を落下させ、50%破壊がおこるエネルギー)は30Kg・cm以

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レフタル酸ジクロライドを真空下100℃以下で除去し、1,10-デカンジオール-テレフタル酸ジクロライド反応物を得た。この反応物はGPC解析及び水で処理した後の中和当量より、1,10-デカンジオール/テレフタル酸ジクロライドの $\frac{1}{2}$ 反応物であることを確認した。

ブロック共重合体の製造

上記反応物1.84g (3.63ミリモル)を用いる以外は実施例-2と同様に反応を行ない(η)0.41のポリフェニレンエーテルブロック共重合体を得た。

物性測定

このものの物性を実施例-1と同様の方法にて測定したところ熱変形温度は200℃、デュボン衝撃強度は12Kg・cm以上であり、またMIは35g/10分であつた。

実施例-4

ポリエステル中間体の製造

(η) 0.46 (\overline{M}_n 23,000) のポリフェニレンエーテル100gと脱水したベンゼン500mlを

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上であつた。また280℃、20Kg荷重で測定したMIは2.1g/10分であつた。

実施例-2

(η)が0.33 (\overline{M}_n 14000) のポリフェニレンエーテルを用い、実施例-1で得たポリテトラメチレングリコール/テレフタル酸ジクロライドの $\frac{1}{2}$ 反応物8.75g (3.63ミリモル)と脱水したビリジン1.18g (14.5ミリモル)を用いる以外は実施例-1と同様の方法で反応を行ない(η)が0.46のポリフェニレンエーテルブロック共重合体を得た。このものの物性を実施例-1と同様の方法にて測定したところ熱変形温度は175℃、デュボン衝撃強度は12Kg・cmまたMIは1.5g/10分であつた。

実施例-3

ポリエステル中間体の製造

1,10-デカンジオールを10倍モルのテレフタル酸ジクロライドと70℃で1時間、ついで120℃で30分間、発生する塩酸ガスを窒素で追い出しながら反応させた。反応終了後過剰のテ

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トリ窒素雰囲気下50℃で攪拌溶解した。これに大過剰のテレフタル酸ジクロライド8.94g (44.0ミリモル)と脱水したビリジン3.56g (44.0ミリモル)を加え、50℃で1時間攪拌、反応した。反応終了後真空下、溶剤のベンゼンを、次いで150℃に昇温し、テレフタル酸ジクロライドを除去し、ポリフェニレンエーテル-テレフタル酸ジクロライド反応物を得た。この反応物はGPC解析及び赤外吸収法による末端基測定により、ポリフェニレンエーテル/テレフタル酸ジクロライドの $\frac{1}{2}$ 反応物である事を確認した。

ブロック共重合体の製造

上記反応物100gと脱水したベンゼン500mlをとり、窒素雰囲気下50℃で攪拌溶解した。これにポリテトラメチレングリコール(MW 2,080)4.58g (2.20ミリモル)及び脱水したビリジン0.70g (8.80ミリモル)を加えた後50℃で1時間攪拌反応した。反応終了後メタノールにて再沈し、洗浄、乾燥して(η)0.55のポリフェニレンエーテルブロック共重合体を得た。

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物性測定

このものの物性を実施例-1と同様の方法にて測定したところ、熱変形温度は180℃、デュボン衝撃強度は30 Kg/cm以上であり、またMIは2.0 g/10分であつた。

比較例-1

(7) 0.46のポリフェニレンエーテル100gとポリテトラメチレングリコール4.53g(2.20ミリモル)をベンゼン溶剤中で溶液ブレンドした。ブレンド後溶剤を留去し、ブレンド物を得た。このものの物性を実施例-1と同様の方法にて測定したところ、熱変形温度は160℃、デュボン衝撃強度は9 Kg/cmであり、またMIは13 g/10分であつた。

比較例-2

(7) 0.46のポリフェニレンエーテルの物性を実施例-1と同様の方法にて測定したところ、熱変形温度は202℃、デュボン衝撃強度は12 Kg/cmであり、またMIは0.8 g/10分であつた。

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外は実施例-5と同様の方法にてポリフェニレンエーテル組成物を得た。このものの物性を実施例-1と同様の方法にて測定したところ、熱変形温度は133℃、デュボン衝撃強度は7.5 Kg/cmであり、またMIは46 g/10分であつた。

特許出願人 三菱油化株式会社
代理人 弁理士 古川 秀利
代理人 弁理士 長谷 正久

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実施例-5

実施例-1で得たポリフェニレンエーテルブロック共重合体50gとハイインパクトポリスチレン(475-D、旭ダウ社製)50gをブラベンダーで250℃にて10分間ブレンドすることによりポリフェニレンエーテル組成物を得た。このものの物性を実施例-1と同様の方法にて測定したところ、熱変形温度は130℃、デュボン衝撃強度は12 Kg/cmであり、またMIは90 g/10分であつた。

実施例-6

実施例-2で得たポリフェニレンエーテルブロック共重合体を用いる以外は実施例-5と同様の方法にてポリフェニレンエーテル組成物を得た。このものの物性を実施例-1と同様の方法にて測定したところ、熱変形温度は131℃、デュボン衝撃強度は10.5 Kg/cmであり、またMIは130 g/10分であつた。

比較例-3

(7) 0.46のポリフェニレンエーテルを用いる以

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PTO 03-3279

Japanese Kokai Patent Application
No. Sho 57[1982]-195122

POLYPHENYLENE ETHER BLOCK COPOLYMER

Ryohei Tanaka et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. MAY 2003
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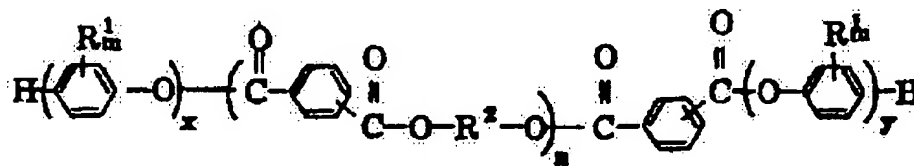
POLYPHENYLENE ETHER BLOCK COPOLYMER

[Porifenirene eteru burokku kyojugotai]

Inventors:	Ryohei Tanaka et al.
Applicant:	Mitsubishi Petrochemical Co., Ltd.
[There are no amendments to this patent.]	

Claim

A type of polyphenylene ether block copolymer represented by the following formula:



(where R¹ groups independently represent a hydrogen atom, halogen atom, hydrocarbon residual group, halo-hydrocarbon residual group, hydrocarbon oxy group, or halo-hydrocarbon oxy group; R² represents a C5-20 alkylene group or polyalkylene polyether with a molecular weight

of 2000 or smaller; m represents the substituting degree and it is an integer in the range of 0-4; n represents an integer in the range of 1-100; and x and y represent the polymerization degree of the polyphenylene ether, and they are integers in the range of 50-250).

Detailed explanation of the invention

Technical background of the invention

Technical field

This invention pertains to a type of polyphenylene block copolymer with improved properties.

Polyphenylene ether resin has excellent electric properties and mechanical properties, and a high thermal deformation temperature. Consequently, it is attractive as a highly useful engineering plastic material. However, it has a high melting point, and poor thermal stability at a high temperature, so that it is hard to perform molding processing in the melt state.

Prior art

As a method for improving the moldability of polyphenylene ether resin, it can be blended with other resins. For example, Japanese Kokoku Patent No. Sho 43[1968]-17812 described a method in which polyphenylene ether is blended with high-impact polystyrene. For this blend, improvement is realized with respect to the moldability and impact strength of the polyphenylene ether resin. The blend has been marketed in the name of Noril [transliteration]. However, the moldability of this blend is still insufficient.

As another method for improving the moldability of polyphenylene ether resin, studies have been made on the addition of a plasticizer. For example, Japanese Kokoku Patent No. Sho 49[1974]-5220 described a method in which the moldability is improved by adding a compound selected from an aromatic organic acid ester, a polyester having an aromatic nucleus, an organic phosphoric ester having an aromatic nucleus, and a chlorinated aromatic hydrocarbon, which have excellent compatibility with polyphenylene ether resin, into polyphenylene ether or a mixture of polyphenylene ether and polystyrene. In this case, however, although addition of the plasticizer improves the moldability, it nevertheless leads to significant degradation in the thermal performance.

Abstract of the invention

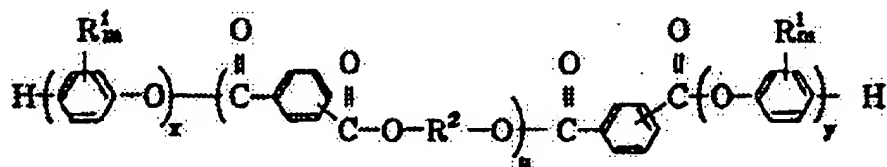
Objective

In order to improve the moldability of polyphenylene ether without degradation in high performance properties, the present inventors have performed extensive studies. As a result, it was found that a polyphenylene ether block copolymer with the following structure has much

better moldability than that of polyphenylene ether resin. In addition, amazingly, it displays improvement also in mechanical strength, especially impact strength.

Gist

This invention provides a type of polyphenylene ether block copolymer represented by the following formula:



(where R^1 groups independently represent a hydrogen atom, halogen atom, hydrocarbon residual group, halo-hydrocarbon residual group, hydrocarbon oxy group, or halo-hydrocarbon oxy group; R^2 represents a C5-20 alkylene group or polyalkylene polyether with a molecular weight of 2000 or smaller; m represents the substituting degree and it is an integer in the range of 0-4; n represents an integer in the range of 1-100; and x and y represent the polymerization degree of the polyphenylene ether, and they are integers in the range of 50-250).

Effects

For the polyphenylene ether block copolymer of this invention, it is possible to improve the moldability with little degradation in the various high performance properties of the polyphenylene ether resin, and, it is possible to improve the mechanical strength, especially impact strength over those of a conventional polyphenylene ether.

Detailed explanation of the invention

1. Polyphenylene ether block copolymer

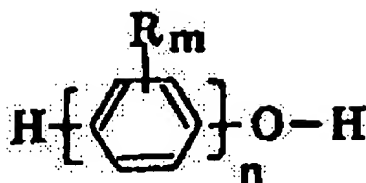
(1) Manufacturing method

The polyphenylene ether block copolymer of this invention can be manufactured easily by means of a reaction between polyphenylene ether and aliphatic dialcohol via an aromatic dicarboxylic acid.

(a) Structural components

Polyphenylene ether

Polyphenylene ether used in forming said polyphenylene ether block copolymer is represented by the following formula:



where substituent R^1 [sic; R] represents a hydrogen, halogen atom, hydrocarbon residual group (especially a C1-12 alkyl group), halo-hydrocarbon residual group (especially a C1-12 halo-alkyl group), hydrocarbon oxy group (especially a C1-12 alkyloxy group), or halo-hydrocarbon oxy group (especially a C1-12 halo-alkyloxy group, and it is preferred that at least two carbon atoms be present between the phenyl group and any halogen that should be bonded to said group). It is preferred that the hydrocarbon or hydrocarbon portion of said group be free of a tertiary- α -carbon atom. m represents the substituting degree, and it is an integer up to 4. N represents the polymerization degree, and it should be in the range of 50-250, or preferably in the range of 100-200. The polyphenylene ether and its manufacturing method are irrelevant to this invention themselves. As needed, one can find them in the following references: US Patent No. 3,257,357, No. 3,306,874, etc. Usually, polyphenylene ether can be manufactured by oxidation coupling of the corresponding phenolic compound. Depending on the positions and types of substituents (see said formula) as well as the polymerization method, it is also possible to obtain types other than 1,4-bonds and copolymers. Such types of polyphenylene ether are also included in this invention as long as the gist of this invention is observed.

The following are examples of polyphenylene ether that can be used in this invention.

Poly(2,6-dimethyl-1,4-phenylene)ether, poly(2-methyl-6-ethyl-1,4-phenylene)ether, poly(2-methyl-6-propyl-1,4-phenylene)ether, poly(2,6-dipropyl-1,4-phenylene)ether, poly(2-ethyl-6-propyl-1,4-phenylene)ether, poly(2,6-dilauryl-1,4-phenylene)ether, poly(2,6-diphenyl-1,4-phenylene)ether, poly(2,6-dimethoxy-1,4-phenylene)ether, poly(2,3,6-trimethyl-1,4-phenylene)ether, poly(2,3,5,6-tetrapropyl-1,4-phenylene)ether, poly(2,6-diethoxy-1,4-phenylene)ether, poly(2-methoxy-6-ethoxy-1,4-phenylene)ether, poly(2-ethyl-5-stearyloxy-1,4-phenylene)ether, poly(2,6-dichloro-1,4-phenylene)ether, poly(2,3-dimethyl-5-chloro-1,4-phenylene)ether, poly(2-methyl-6-phenyl-1,4-phenylene)ether, poly(2,6-dibenzyl-1,4-phenylene)ether, poly(3-chloro-1,4-phenylene)ether, poly(3,5-diethyl-1,4-phenylene)ether, poly(3-ethoxy-1,4-phenylene)ether, poly(2-chloro-1,4-phenylene)ether, poly(2,5-dibromo-1,4-phenylene)ether, etc.

Aliphatic dialcohol

Examples of aliphatic dialcohol include alkylene diol and polyalkylene glycol. When the chain is too short, the effect becomes less significant. On the other hand, if the chain is too long, the thermal performance degrades. The molecular weight is preferably in the range of 100-2000. Specific examples include 1,8-octanediol, 1,10-decanediol, polyethylene glycol, polytetramethylene glycol, etc.

Aromatic dicarboxylic acid

Examples of aromatic dicarboxylic acids include terephthalic acid, isophthalic acid, ortho-phthalic acid, etc. Among them, terephthalic acid is preferred.

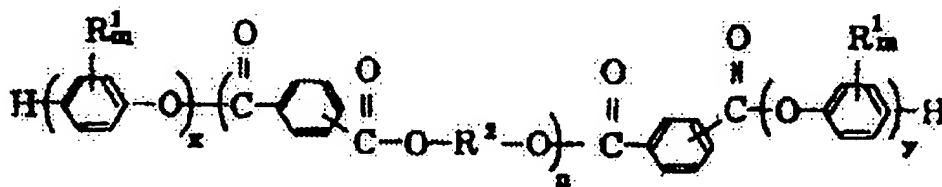
In this case, instead of the acid chloride of the aromatic dicarboxylic acid, one may make use of the diethylether of the aromatic dicarboxylic acid or the aromatic dicarboxylic acid itself as is.

(b) Manufacturing conditions

Generally speaking, the following three methods may be adopted in manufacturing a polyphenylene ether block copolymer of this invention.

In the first method, an aliphatic dialcohol is reacted with an equal or more molar amount of the acid chloride of an aromatic dicarboxylic acid to form a reaction intermediate body having acid chloride at its two terminals. The molecular weight of the intermediate body can be controlled by means of the charge ratio of the aliphatic dialcohol and the acid chloride of an aromatic dicarboxylic acid. Then, the reaction intermediate body having acid chloride at its two terminals prepared in the aforementioned way is reacted with polyphenylene ether to form the desired polyphenylene ether block copolymer.

In the second method, polyphenylene ether is reacted with the acid chloride of an aromatic dicarboxylic acid to form a polyphenylene ether intermediate body having an aromatic carboxylic acid chloride at its terminals, and it is reacted with aliphatic dialcohol to form the desired polyphenylene ether block copolymer. For the polyphenylene ether block copolymer prepared in this method, n is 1 in the following formula:



In the third method, the acid chloride of an aromatic dicarboxylic acid in the presence of polyphenylene ether is reacted with aliphatic dialcohol to form the desired compound.

As in the first method, in the second and third methods, instead of the acid chloride of an aromatic dicarboxylic acid, one may make use of a dimethyl ester of an aromatic dicarboxylic acid or an aromatic dicarboxylic acid itself as is.

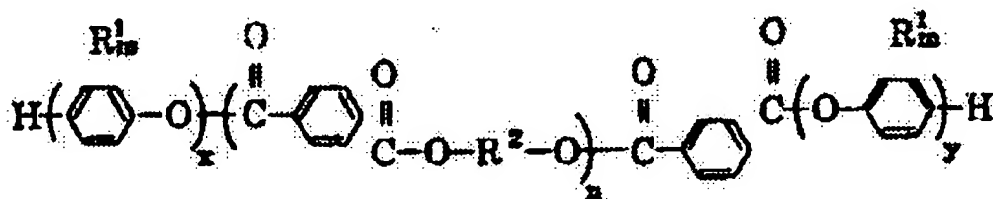
Any of said three methods may be used in manufacturing a polyphenylene ether block copolymer. However, compared with the first and second methods, the third method has a tendency of a broader distribution of molecular weight.

As far as the reaction conditions are concerned, in the step of manufacturing of the reaction intermediate body and in the step of obtaining the polyphenylene ether block copolymer, when terephthalic acid chloride is used in benzene or another dissoluble solvent, reaction is performed at 30-100°C for 1-8 h with agitation. In this case, as needed, one may also make use of pyridine, triethylamine, and other amines.

2. Characteristics of the block copolymer

For the polyphenylene ether block copolymer prepared in this way, with little degradation in the high performance properties of polyphenylene ether resin, it is possible to improve the moldability significantly, and it is possible to significantly improve the mechanical strength, especially the impact strength.

The polyphenylene ether block copolymer of this invention is a copolymer represented by the following formula:



(where R [sic; R¹] groups independently represent a hydrogen atom, halogen atom, hydrocarbon residual group, halo-hydrocarbon residual group, hydrocarbon oxy group, or halo-hydrocarbon oxy group; R² represents a C5-20 alkylene group or polyalkylene polyether with a molecular weight of 2000 or smaller; m represents the substituting degree and it is an integer in the range of 0-4; n represents an integer in the range of 1-100; and x and y represent the polymerization degree of the polyphenylene ether, and they are integers in the range of 50-250).

In the aforementioned formula, x and y represent the polymerization degree of the polyphenylene ether, and they are integers in the range of 50-250, or preferably in the range of

100-200. If smaller than 50, the electric characteristics, a characteristic feature of polyphenylene ether, degrade. On the other hand, if over 250, improvement of the moldability is less significant.

In addition, n represents an integer in the range of 1-100. If it is larger than 100, the heat resistance degrades. Also, when R^2 represents a polyalkylene polyether, one may use a polyalkylene polyether with molecular weight of 2000 or smaller, or preferably in the range of 500-1000.

3. Blends with other resins

Said polyphenylene ether block copolymer may be used alone, or as a blend with a polystyrene based polymer, or as a blend with a resin composition made of a polyphenylene ether and a polystyrene based polymer.

Because the copolymer of this invention has improved moldability, it can be used alone. However, in consideration of the cost, it is preferred that it be used as a blend with a polystyrene based polymer.

Also, the composition of the polyphenylene ether block copolymer of this invention may contain other additives, such as a plasticizer, pigment, flame retarding agent, reinforcing agent, such as glass filaments or fibers, stabilizer, etc.

In the following, this invention will be explained in more detail with reference to application examples.

Application Example 1

Manufacturing of polyester intermediate body

Polytetramethylene glycol having OH at two terminals (MW2080) was reacted with 10-fold (molar amount) terephthalic acid dichloride at 50°C for 1 h, and then at 120°C for 30 min, while the hydrochloric acid gas generated in the process was exhausted. After completion of the reaction, the excess terephthalic acid dichloride was removed in vacuum at 100°C or lower temperature, forming a reaction product of polytetramethylene glycol-terephthalic acid chloride. According to GPC analysis and from the neutralization equivalent after treatment with water, the product was found to be the 1/2 reaction product of polytetramethylene glycol/terephthalic acid dichloride.

Manufacturing of block copolymer

100 g of polyphenylene ether with $[\eta]$ of 0.46 (chloroform at 30°C) (\overline{Mn} of 23,000) and 500 mL of dehydrated benzene were agitated for formation of a solution in a nitrogen atmosphere at 50°C. Then, 5.31 g (2.20 mmol) of said reaction product and 0.70 g (8.80 mmol) of dehydrated pyridine were added into the solution, followed by agitation at 50°C for 1 h for

reaction. After end of the reaction, methanol was used for re-precipitation, followed by washing and drying to form a polyphenylene ether block copolymer. It has $[\eta]$ of 0.58.

Measurement of properties

Specimens were prepared using a press. The thermal deformation temperature under a load of 18.6 kg was measured, and was found to be 183°C. The DuPont impact strength was found to be 30 kg-cm or higher (Test was performed by setting a specimen (thickness of 0.6 mm) between a hammer (12.5 mm in diameter) and a table having a dent in it, and the hammer with a prescribed weight (300 g) was allowed to fall. The energy corresponding to 50% damage was taken as the DuPont impact strength). Also, the MI measured at 280°C and under a load of 20 kg was found to be 2.1 g/10 min.

Application Example 2

A polyphenylene ether block copolymer with $[\eta]$ of 0.46 was prepared in a reaction performed in the same way as in Application Example 1, except that polyphenylene ether with $[\eta]$ of 0.33 (\overline{Mn} of 14,000) was used, and 8.75 g (3.63 mmol) of the 1/2 reaction product of polytetramethylene glycol/terephthalic acid dichloride and 1.18 g (14.5 mmol) of dehydrated pyridine were used. The properties of the obtained product were measured in the same way as in Application Example 1. It was found that the thermal deformation temperature is 175°C, the DuPont impact strength is 12 kg-cm, and the MI is 15 g/10 min.

Application Example 3

Manufacturing of polyester intermediate body

1,10-decanediol was reacted with 10-fold (molar amount) terephthalic acid dichloride at 70°C for 1 h, and then at 120°C for 30 min, while the hydrochloric acid gas generated in the process was exhausted. After completion of the reaction, the excess terephthalic acid dichloride was removed in a vacuum at 100°C or lower temperature, forming a reaction product of 1,10-decanediol-terephthalic acid dichloride. According to GPC analysis and from the neutralization equivalent after treatment with water, the product was found to be the 1/2 reaction product of 1,10-decanediol/terephthalic acid dichloride.

Manufacturing of block copolymer

A polyphenylene ether block copolymer with $[\eta]$ of 0.41 was obtained in a reaction performed in the same way as in Application Example 2, except that 1.84 g (3.63 mmol) were used.

Measurement of properties

The properties were measured using the same methods as those in Application Example 1. It was found that the thermal deformation temperature is 200°C, the DuPont impact strength is 12 kg-cm or higher, and the MI is 35 g/10 min.

Application Example 4

Manufacturing of polyester intermediate body

100 g of polyphenylene ether with $[\eta]$ of 0.46 (\overline{M}_n of 23,000) and 500 mL of dehydrated benzene were agitated for solution formation in a nitrogen atmosphere. A significantly excess amount (8.94 g (44.0 mmol)) of terephthalic acid dichloride and 3.56 g (44.0 mmol) of dehydrated pyridine were added into it, followed by agitation for reaction at 50°C for 1 h. After completion of the reaction, benzene in the solvent was removed in a vacuum, and the temperature was raised to 150°C to remove terephthalic acid dichloride, forming a polyphenylene ether-terephthalic acid dichloride reaction product. According to GPC analysis and terminal group measurement using IR absorption method, the reaction product was found to be a 1/1 reaction product of polyphenylene ether/terephthalic acid dichloride.

Manufacturing of block copolymer

100 g of said reaction product and 500 mL of dehydrated benzene were agitated for solution formation at 50°C in a nitrogen atmosphere. After 4.58 g (2.20 mmol) of polytetramethylene glycol (MW2,080) and 0.70 g (8.80 mmol) of dehydrated pyridine were added, the mixture was agitated for reaction at 50°C for 1 h. After completion of the reaction, methanol was used to perform re-precipitation, followed by washing and cleaning to form a polyphenylene ether block copolymer with $[\eta]$ of 0.55.

Measurement of properties

The properties were measured using the same methods as those in Application Example 1. It was found that the thermal deformation temperature is 180°C, the DuPont impact strength is 30 kg-cm or higher, and the MI is 2.0 g/10 min.

Comparative Example 1

100 g of polyphenylene ether with $[\eta]$ of 0.46 and 4.53 g (2.20 mmol) of polytetramethylene glycol were dissolved in a benzene solvent to form a solution blend. After blending, the solvent was distilled off to obtain a blend. The properties were measured using the same methods as those in Application Example 1. It was found that the thermal deformation temperature is 160°C, the DuPont impact strength is 9 kg-cm, and the MI is 13 g/10 min.

Comparative Example 2

For polyphenylene ether with $[\eta]$ of 0.46, the properties were measured using the same methods as those in Application Example 1. It was found that the thermal deformation temperature is 202°C, the DuPont impact strength is 12 kg-cm, and the MI is 0.8 g/10 min.

Application Example 5

50 g of polyphenylene ether block copolymer obtained in Application Example 1 and 50 g of high-impact polystyrene (475-D, product of Asahi Dow Co., Ltd.) were blended using a Brabender blender at 250°C for 10 min to form a polyphenylene ether composition. The properties were measured using the same methods as those in Application Example 1. It was found that the thermal deformation temperature is 130°C, the DuPont impact strength is 12 kg-cm, and the MI is 90 g/10 min.

Application Example 6

A polyphenylene ether composition was prepared in the same way as in Application Example 5, except that the polyphenylene ether block copolymer prepared in Application Example 2 was used in this case. The properties were measured using the same methods as those in Application Example 1. It was found that the thermal deformation temperature is 131°C, the DuPont impact strength is 10.5 kg-cm, and the MI is 130 g/10 min.

Comparative Example 3

A polyphenylene ether composition was prepared in the same way as in Application Example 5, except that polyphenylene ether with $[\eta]$ of 0.46 was used in this case. The properties were measured using the same methods as those in Application Example 1. It was found that the thermal deformation temperature is 133°C, the DuPont impact strength is 7.5 kg-cm, and the MI is 46 g/10 min.